PRODUCTION OF METALLIC POTASSIUM BY THE VACUUM-THERMIC METHOD

- USSR -

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FOREWARD

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Authors' Note: This work was conducted in the experimental workshop of the Dneprovsk Aluminum Plant by a group of scientists from this workshop and also by the associates of the All-Union Aluminum and Magnesium Institute (VAMI - Vsesoyuznyy Aluminiyevo-magniyevyy Institut) V. M. Kozlov and D. N. Chemukov.

- Among the known processes for producing potassium[1] particular interest has been shown to the vacuum-thermic processes which have gained wide acceptance in recent years for the production of a number of alkali and alkaline earth metals[2].

The basis of the vacuum-thermic processes for the production of potassium involve the reduction of potassium chloride in a vacuum by other metals or alloys (metallothermal process) or by calcium carbide (the carbide-thermal process). (P. V. Gel'd et al[3] has reported on the experiments involving the reduction of potassium chloride by calcium carbide.)

Laboratory tests have been conducted by N. M. Nikolayshvilli[4] on the reduction of sodium and potassium chlorides by silicon alloys. Further, V. M. Gus'kov, N. M. Zuyev and A. I. Voynitskiy[5] have studied in great detail the reduction of potassium chloride by aluminum and by silicon alloys, and indicated the possibility of producing potassium by this method.

On the basis of the results from these experiments the authors have written this paper. The reducing agents used were ferrosilicon and aluminum-silicon. (Initially the experiments were performed with calcium carbide and the first portion of them were conducted together with researchers from UNIKhim /Ural Scientific Research Chemical Institute/.

Theoretical Bases of the Process

In order to estimate and evaluate the various vacuum-thermic processes for the reduction of potassium chloride, the equilibrium vapor tensions of potassium and the energy consumptions during the reduction process were determined. In view of the absence of sufficiently accurate data on the composition of the end products of the condensation phase, the fundamental chemical reactions were used for calculations without considering the possibility of some side processes. The thermochemical data used during the calculations were taken from the literature [6-8].

As a basis for calculation the following reactions were considered:

for the carbide-thermal reduction

$$2KCl \neq CaC_2 = CaCl_2 \neq 2C \neq 2K; \tag{1}$$
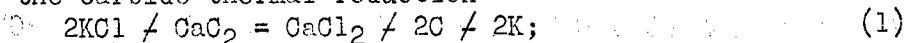
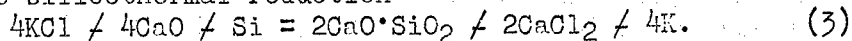for the aluminothermal reduction (present during the reduction of potassium chloride by aluminum-silicon (Si-Al))

$$18KCl \neq 14CaO \neq 6Al = 5CaO \cdot 3Al_2O_3 \neq 9CaCl_2 \neq 18K \tag{2}$$

for the silicothermal reduction

$$4KCl \neq 4CaO \neq Si = 2CaO \cdot SiO_2 \neq 2CaCl_2 \neq 4K. \tag{3}$$
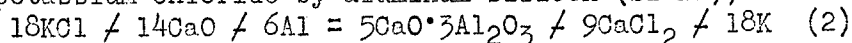
Having determined the values for these reactions by simple calculations: the free energy F in the temperature range 1123-1323 K, the equilibrium constants K_p, the equilibrium vapor tensions of potassium P_K and the logarithms of the latter (Table 1), we found the following logarithmic relationships of the equilibrium vapor tensions to the temperature:

for reaction (1)
$$\lg P_K = 6.79 \cdot 6880/T$$
for reaction (2)
$$\lg P_K = 8.00 \cdot 7810/T$$
for reaction (3)
$$\lg P_K = 8.4 \cdot 9186/T.$$

Table 1

Free Energy, Equilibrium Constant and Equilibrium Vapor Tensions for Potassium

Charact-eristics	Temperature		Silico-thermal reduction	Carbide-thermal reduction	Alumino-thermal reduction
	K	C			
F, cal.	1123	850	55 040	23 070	168 504
	1223	950	44 840	19 170	125 504
	1323	1050	34 990	15 370	84 504
K_p at ,	1123	850	$10^{-5.7}$	$10^{-3.7}$	10^{-33}
	1223	950	$10^{-8.0}$	$10^{-3.5}$	10^{-25}
	1323	1050	$10^{-5.73}$	$10^{-3.57}$	$10^{-12.8}$
P_K, mm on Hg Bulb	1123	850	1,6	4,4	11,38
	1223	950	7,6	14,5	43,3
	1323	1050	27,2	40,7	127,5
$\lg P_K$	1123	850	0,2	0,64	1,055
	1223	950	0,88	1,16	1,635
	1323	1050	1,43	1,61	2,105

These relationships have been graphically presented in Figure 1, where in addition, the saturated vapor tension curve of potassium chloride has been plotted. It should be noted that the equilibrium tension for the silicon-thermal process is lower than for the other two

processes and for the given section almost coincides with the tension of saturated vapors of potassium chloride. This explains the obtaining in our tests of considerably lower yeelds of potassium during the silicon-thermal process than during the carbide-thermal process, until means were found for increasing the velocity of the reduction reaction of potassium chloride by silicon and methods for decreasing the sublimation of potassium chloride (see below). The theoretical quantity of energy, necessary to produce potassium by the silicon-thermal method at the optimal reaction temperature, 950 C, in agreement with equation (3) amounts to the sum of heat lost in heating up the initial reaction products to the process temperature, and the heat effect of the reaction at a given temperature.

It is not difficult to calculate the first item

$$\bar{}(H_{1223}-H_{298}) = 135,210 \text{ cal.}$$ while the heat effect of the reaction $\triangle H_{1223} = 201,870$ cal.

The total theoretical heat consumption for the process:

$$\bar{}(H_{1223}-H_{298}) + H_{1223} = 337,090 \text{ cal.}$$

Thus, the theoretical specific consumption of electric energy for 1 kg of potassium is 2.5 kilowatt-hours.

Experimental

Experiments were conducted on a semi-industrial scale. The apparatus used allowed a 150-300 kg charge to loaded at once to produce 20-40 kg of metallic potassium.

The technology of the vacuum-thermic production of potassium consists of two basic processes: preparing the charge in the form of briquettes and correct vacuum-thermic reduction of the potassium chloride. The preparation of the briquette charge was done in the usual manner and therefore did not cause any difficulty; but for reducing potassium chloride there was required the development both of the technology of the process and its operating conditions as well as the equipment. There were serious difficulties encountered with this portion of the work since simultaneously with the reducing reaction there occurs an intensive sublimation of the salt, which leads: to a lowering of the velocity of the reaction because of the decrease of KCl concentration in the charge; to clogging of the equipment by the condensed salt as a result of which the vapor phase pressure in the reaction field increases and the reaction is stopped; to "sticking" of the metal in the salt condensate. Thus the task of the experiments was to find ways to increase the velocity of the reducing reaction and to slow down the sublimation of the salt, and also to provide for the distinct condensation of the salt vapors and metal vapors for the production of the pure metal.

The Charge. The starting materials used were potassium chloride containing up to 4% NaCl, limestone and ferrosilicon (Si-72.3%).

In order not to introduce gases into the reaction apparatus which disturb the vacuum and react with the reaction products, it is necessary to practically completely dehydrate and de-

carbonize the initial raw materials. For this purpose potassium chloride was calcined at 200 - 300° and later crushed. The limestone was fired in a rotating furnace at 1200 - 1300°. The salt, lime and ferrosilicon were ground up in a ball mill with a peripheral diffusion to a grinding fineness of minus 60 - 80 mesh.

Further components of the charge were measured out in determined proportions and were mixed in a cylindrical mixer. The charge was formed in automatic tablet presses into cylindrical briquettes with a 75 mm diameter and height of 30-40 mm, which possessed sufficient mechanical strength.

The reaction apparatus. The reduction process is performed in a vertical vacuum retort-furnace (Figure 2) in which the steel retort placed in the jacket 2 with a counter vacuum was the electrical resistance element. The condenser 5 with a cavity tank for potassium was attached to the lower part of the retort. Above it was the condenser for salt 4 with a salt-apron. The briquettes were loaded from above in a ring configuration between the walls of the retort and the central perforated pipe 3. The latter served as the channel through which salt and metal vapors proceed to the condenser. The salt condenser was heated higher (400-800) than the tank for potassium (60 - 100). Owing to the various condensation temperatures the salt from the vapor phase is condensed on the higher heated surface in the tank and the metal vapor on the lower.

Experimental Methods and Operating procedures. Before loading of the briquettes, the temperature in the retort was 810 - 850. Later during the loading it went down to 650 - 700. In the first period of the process (heating up to 780), the volatile residues (moisture, CO_2, etc.) are eliminated and owing to this the vacuum drops; later it increases according to the degree of heating of the charge and removal of gases. However the remaining pressure is maintained not lower than 6-8 mm (Hg bulb due to which the salt almost does not sublimate.

Later, when the charge has been heated up to the reaction temperature (780 - 800), the vacuum is sharply increased (to 0.5 - 0.8 mm). This provides a higher reaction velocity, due to which a considerable quantity of the salt is reduced, not evaporated. From the moment the current is turned on to the completion of the process takes 8 hours.

During this time the temperature on the walls of the retort is brought up to 950 - 960, the residual vacuum in the retort – to 0.3 - 0.5 mm. Upon completion of the process the current is switched off and the furnace is unloaded in the following order.

For the sake of safety in further operations, dehydrated mineral oil, forming a protective layer on the metal, is sucked into the condenser. Later by admitting air into the furnace the vacuum was removed, the condenser with metal is removed and the condenser with the salt was withdrawn from the furnace (in a number of cases the condenser with the salt was not removed and the salt in it was knocked out). Further

the upper cover was removed and the residue of the charge was
dumped into a trolley placed under the retort, by gradually
raising and pulling the central pipe. After this the empty
condensers were arranged and the retort was loaded for another
cycle.

Discussion of the Results

The first series of tests with a ferrosilicon charge
did not yield satisfactory results. Yields of potassium amounted
to 15 - 35% when loaded into the containers. It was not possible
to raise them neither by increasing the double relationships of
ferrosilicon to potassium chloride nor by increasing the process
time to 24 hours. The same thing was observed when the charge was
loaded immediately into the retort. In this case the process time
was approximately 8 hours, since the longer process was proved to
be inefficient. Later tests were set up in which ferrosilicon and
calcium oxide were crushed to minus 200 mesh to increase the activity
of the charge. Nevertheless even this measure did not help. The
yields of potassium and other characteristics of the process remained
low as before, even with a large surplus of reducing agent.

Simultaneously during the reduction of potassium chloride
by calcium carbide under analogous conditions the yields of
potassium reached 55 - 60%.

Since during the silicon-thermal reduction of potassium
chloride the equilibrium vapor tensions of potassium almost
equal the saturated vapor tensions of KCl (see Figure 1) the
authors supposed that the basic reason for the low potassium
yields is the low velocity of the reduction reaction and that
because of this velocity a considerable quantity of the salt
was being sublimated, not being involved in it.

To increase the velocity of the reaction the addition
(5 and 9%) of calcium fluoride was introduced into the charge
in the second series of tests. The relationship of the
reducing agent to the salt in the charge was taken as equal to
0.5, since it was seen from the previous tests that an increase
in this relationship does not improve the yield. The relation-
ship of the lime to salt was taken as equal to 0.77. From the
results of these tests (Table 2) it can be seen that a 5% fluoride
additive aids in increasing the process characteristics. The yield
of potassium rose from 15 - 35 to 47.7 - 62.7%; the specific
consumption of reducing agent correspondingly dropped from
5.7 - 2.8 to 2.0 - 1.5 kg/kg.

The specific consumption of electrical energy amounted to
14.9 - 19.8 kw-hour/kg of potassium at the terminals of the
furnace which is many times lower than in the tests without the
fluoride additive. As can be seen from the tabular data an 8 -
hour process is sufficient.

Table 2

Results of Tests with Ferrosilicon and Calcium Fluoride Additive

Length of Test, hours	Load of Briq., kg	Yield of Potassium kg	%	Specific Consumption, kg/ kg of potassium Reducing agent	Charge	Specific Consumption of electrical energy at the retort terminals, kw-hours/kg of potassium
8,0	232	25,2	49,8	1,9	9,2	—
8,0	235	24,4	47,7	2,0	9,6	—
8,0	229	28,0	56,0	1,7	8,2	18,8
8,0*	225	27,6	58,5	1,6	8,15	17,8
8,0	222	24,7	51,0	1,8	8,9	19,6
10,0	238	32.8	62.7	1,5	7,25	14,9
10,0	227	25,2	50,7	1,9	9,0	19,8
8,0*	243	31,1	61,2	1,5	7,8	16,1
8,0	233	29,4	58,0	1,6	7,9	17,6
8,0	238	32,2	62,1	1,5	7,4	16,5

It should be noted that the fluoride additive of 5% aids the
scattering of charge remainders which substantially facilitates
their discharge at 900 – 950'. The 9% fluoride additive, conversely,
aggravates discharge since the residues become viscous under
this condition. In addition the increase of CaF_2 in the charge
from 5 to 9% does not improve the potassium yield.

Great interest has been shown to aluminum-silicon alloy as
the reducing agent for the vacuum-thermic production of potassium.
Under known conditions, the production of this alloy is comparatively
cheap and it can compete with ferrosilicon. Aluminum-silicon alloy
containing equal amounts of aluminum and silicon were used in our
experiments. From the results of the experiments (Table 3) it can
be seen that aluminum-silicon as as a reducing agent provides
satisfactory process characteristics. The fluoride additive for the
aluminum-silicon charge is also beneficial, but in this instance its
effect is less significant than for the ferrosilicon charge. This
evidently, is explained by the fact that the reaction with the aluminum
portion of the reducing agent proceeds at a higher velocity than with
the silicon.

Table 3

Results of Tests with Aluminum Silicon
(Eight Hours Duration)

Composition of charge, % Salt	Lime	Reducing agent	Charge Calcium Fluoride	Charge load, in kg	Yield of potassium kg	%	Sp. consumption kg/kg of potas. Reducing agent	Charge	Sp. Consumption of energy, kw-hour/kg of potassium
52,1	15,0	32,9	none	204	22,0	39,3	1,4	9,3	20,4
52,1	15,0	32,9	none	236	28,3	44,0	1,2	8,3	16,2
49,5	14,3	31,5	4,7	235	36,1	59,5	0,93	6,5	14,5
49,5	14,3	31,5	4,7	252	38,1	58,5	0,94	6,6	13,0

Upon comparing the process characteristics obtained with ferrosilicon and aluminum silicon (Table 4), it should be noted that even with a somewhat lower yield of potassium the specific consumption of aluminum silicon is considerable lower than of the ferrosilicon. This is very important since the reducing agent is the most expensive component in the charge. The specific consumption of aluminum silicon charge is considerably lower which in turn is a substantial advantage.

Table 4

Characteristics of the Process for the Ferrosilicon and Aluminum Silicon Charges

Item	Charge	
	Fe-Si	Al-Si
Duration of process, hours	8	8
Single load of charge, kg	240	243
Yield, kg:		
Metal	32,0	37,1
Salt	19,2	--
Yield of metal, %	62,0	59,0
Recovery of salt, %	19,2	--
Specific consumption, kg/kg metal:		
Charge	7,5	6,55
Reducer	1,5	0,935
Specific consumption of energy at terminals of retort, kwatt-hours	15,8	13,75

The quality of the prepared metal was determined by chemical analysis for impurities of sodium, calcium and chlorine. The quantity of sodium in the metal amounted to 3% on an average. The admixture, NaCl in the inital salt, which is reduced to metallic sodium and is condensed along with potassium, is the source of contamination of the potassium by sodium. It has been observed that the sodium content in the product increases with a decrease in the potassium yield. Admixtures of calcium and chlorine, as a rule, were not observed in the metal.

Thus, the results of conducted works in particular on the technology and equipment of the process, and also on safety engineering, are a reliable basis for the introduction of the silicon-thermal process for the production of potassium on an industrial scale.

The production diagram of the process is outlined in Figure 3. It consists of the following basic operations; calcination of the potassium chloride and firing the limestone, crushing the components of the charge, their mixing and pressing into briquettes, vacuum-thermic reduction of the KCl.

The vertical vacuum-retort furnace of a given type with much larger measurements can be recommended for the chief link of the diagram in the reduction process.

In the field of apparatus designing in the process there should be noted the development of construction principles for the reaction vacuum-thermic apparatus for the production of potassium, namely, a vertical ring-shaped distribution of the charge, which can be fired from one or two sides; the utilization of the middle of the reaction area (a ring) as collector and channel through which vapors are directed into the condensers; the sequential disposition of the salt condenser having a maze of baffles and the condenser for the metal in corresponding temperature zones. On the basis of the use of these principles further development of the reaction apparatus to greater cyclic productivity is possible.

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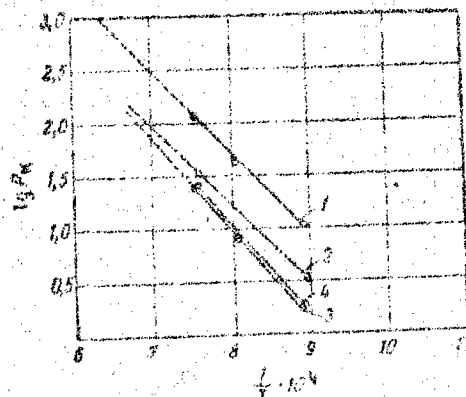
Fig. 1 Logarithmic curves of the dependence of the equilibrium
vapor tension on the temperatures of potassium for the reduction
of KSi , and KSi vapor tension:
1-Alumino-thermic reduction; 2-Carbide-thermic reduction;
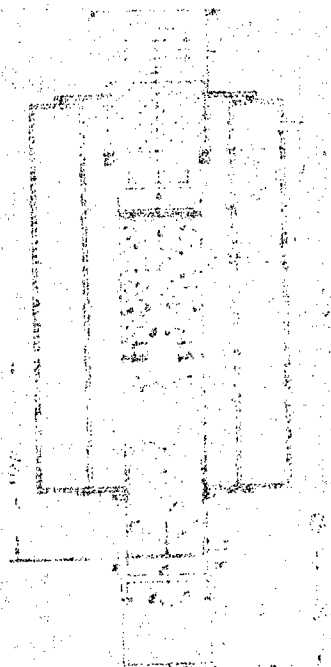3-Silicon-thermic reduction; 4-Saturated vapor tension for KSi.

Fig. 2 Sketch of a vertical vacuum retort furnace with charge loaded
in the retort: 1-Vacuum retort; 2-Counter-vacuum jacket with
lining; 3-Central extendable loading tube; 4-Salt condenser;
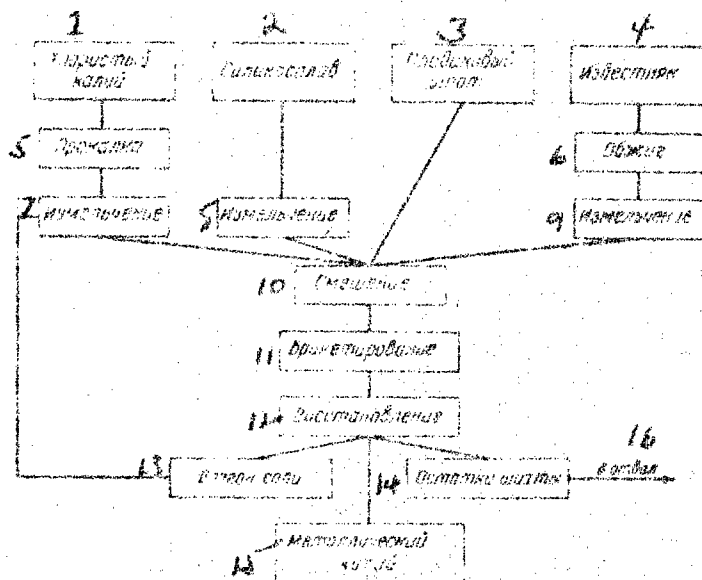5-Metallic potassium condenser.

Fig. 3 Production diagram of the silicon-thermo process
for obtaining potassium

1-Potassium chloride	10-Mixing
2-Silicon alloy	11-Forming into
3-Fluorspar	Briquettes
4-Limestone	12-Reduction
5-Calcination	13-Sublimation
6-Firing	of Salt
7-Crushing	14-Charge Residue
8-Crushing	15-Metallic Potassium
9-Crushing	16-To refuse

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